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SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF SPINEL-TYPE PIGMENTS

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The process of producing spinel-type pigments from a mixture of Al_2O_3 and Co_2O_3 with aluminum powder ASD-4 and MgO and ZnO additives by the method of self-propagating high-temperature synthesis (SHS) is investigated. A blue and an ultramarine pigment are obtained. Their phase composition, IR spectra, and structural and color characteristics are studied. It is demonstrated that the SHS method is promising for producing heat-resistant spinel-type pigments of a blue-sky-blue color range.

Spinel-type pigments are commonly used in decorating porcelain and other ceramic products, as a consequence of their high thermal resistance. They represent complex oxides with the general formula $A^{2+}B^{3+}O_4$ containing two cations (A, B), one of which has the degree of oxidation 2+ and the other, 3+. If the bivalent metal is either cobalt or zinc and magnesium partly replacing cobalt and the trivalent ion is aluminum, then the resulting pigments form a blue-sky-blue color range. The synthesis of such spinels is usually carried out by firing their metal oxides or salts in a furnace at high temperatures (1300 – 1400°C).

If metallic aluminum powder is used as an initial component, spinel can be synthesized by the method of self-propagating high-temperature synthesis (SHS). RF patents Nos. 2029745 and 2120918 demonstrate the fundamental possibility of producing ceramic pigments using this method.

The purpose of this study is to produce pure-tone spinel-type pigments of blue and sky-blue shades by the SHS method and to study their phase and structure formation processes.

Pigments were produced using Al_2O_3, Co_2O_3, ZnO, MgO, and aluminum powder ASD-4. Synthesis was performed on a constant-pressure plant.

The microstructure of samples was investigated using light microscopy (MIM-8, Unimet) and scanning electron microscopy (Camebax); the same instrument performed the x-ray microspectral analysis. The thermal oxidation of materials was studied on a Q-1500 derivatograph in the temperature interval of 25 – 1000°C in air with a heating rate of 10 K/min. The maximum reaction temperature was measured using a tungsten-rhenium thermocouple. The obtained pigments were identified by x-ray phase analysis using a DRON-UM1 diffractometer (filtered CoK_α radiation) and infrared spectroscopy[2] in a range of 4000 – 400 cm^{-1} on a Nicolet-5700 IR-Fourier spectrometer with a diffuse-reflection instrument in KBr. The characteristics of pigment colors were calculated based on reflection spectra recorded on a Spekord M-40 spectrophotometer in the wavelength range 350 – 800 nm.

Blue pigments were synthesized in the system $CoO – Al_2O_3$. Based on x-ray phase analysis data, apart from cobalt-aluminum spinel $CoAl_2O_4$, the products of synthesis contain aluminum oxide and cobalt. A study of the microstructure of the product also indicates the presence of a fourth phase: a thin CoO film on metallic cobalt particles, which is not identifiable by x-ray phase analysis. The x-ray microspectral analysis corroborates the presence of cobalt oxide.

Thermal analysis indicates that in both cases a phase transformation takes place at 660°C related to the melting of aluminum; next, at 915°C (system $CoO – Al_2O_3$) and 920°C (system $ZnO – CoO – Al_2O_3$), we observe an endothermic effect (DTA curve) and a weight loss (DTG curve) caused by the decomposition of Co_3O_4 into CoO and O_2. In the second system, the weight increment process is overlapped by another local process, i.e., a weight loss accompanied by an endothermic effect at 940°C, which is presumably related to the formation of solid solution $CoO \cdot xZnO$. The presence of the solid solution (pigment: green cobalt) is corroborated by optical analysis methods. Malachite-green inclusions are visible with a microscope. The variation of the maximum temperature during the SHS process is represented in Fig. 1. The

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[2] IR spectroscopic studies were performed on the equipment of the Scientific-Analytical Center at the Tomsk Polytechnical University.

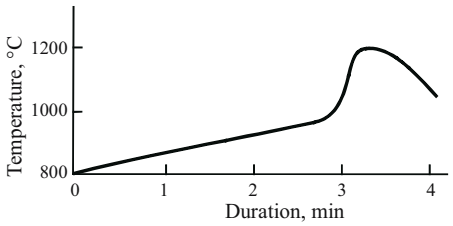

Fig. 1. Thermogram of $CoO - Al_2O_3$ system.

following reactions may take place in the course of synthesis:

$$6Co_2O_3 \xrightarrow{300-600\,^\circ C} 4Co_3O_4 + O_2\uparrow;$$

$$4Al + 3O_2 = 2Al_2O_3;$$

$$2Co_3O_4 \xrightarrow{900\,^\circ C} 6CoO + O_2\uparrow;$$

$$2Co_2O_3 \xrightarrow{1150-1200\,^\circ C} 4CoO + O_2;$$

$$CoO + Al_2O_3 \xrightarrow{925\,^\circ C} CoAl_2O_4.$$

The summary reaction is

$$6Co_2O_3 + 4Al + 10Al_2O_3 = 12CoAl_2O_4.$$

In the case of an oxygen deficit we have

$$Co_3O_4 + 2Al \rightarrow CoAl_2O_4 + 2Co.$$

However, the color of the obtained pigment is dark blue. To improve its color characteristics, ZnO was introduced in the $CoO - Al_2O_3$ system. According to x-ray phase analysis data, in partial replacement of cobalt oxide by zinc oxide, zinc spinelides are formed. The synthesized pigment has an ultramarine color. The following reactions take place in the synthesis:

$$ZnO + Al_2O_3 = ZnAl_2O_4;$$

$$ZnO + Co_2O_3 \xrightarrow{800\,^\circ C} ZnCo_2O_4;$$

$$2ZnCo_2O_4 \xrightarrow{900-1000\,^\circ C} 4CoO + 2ZnO + O_2.$$

IR spectroscopy analysis established that the introduction of ZnO decreases the content of free alumina (Fig. 2). Thus, the peak at 884 cm^{-1} caused by the stretching vibrations of the bond $\nu(Al - O)$ perceptibly decreases. In addition to the absorption bands in the ranges of 569 and 672 cm^{-1} caused by the vibrations of the bonds of octahedral aluminum AlO_6 and tetrahedral cobalt CoO_4, respectively, the second sample exhibits vibrations at 532 and 465 cm^{-1} due to the bonds of tetrahedral zinc ZnO_4 [1, 2]. An additional introduction of magnesium oxide into the system leads to a complete binding of free alumina, whose vibrations in the IR spectrum are absent. We observe the classical IR spectrum of a spinel structure, which typically has ab-

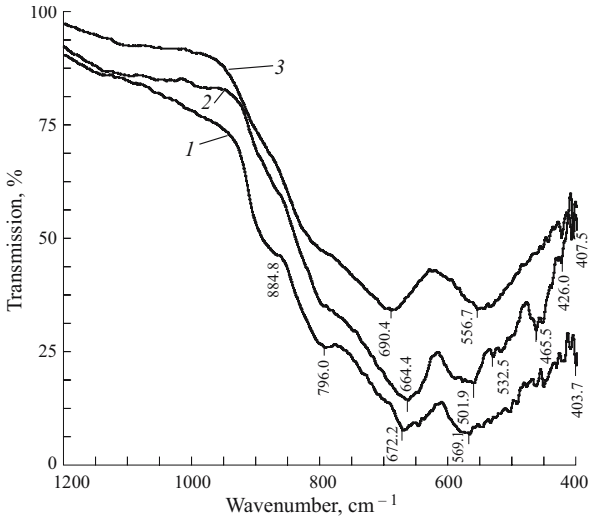

Fig. 2. IR spectra of pigments produced in systems $CoO - Al_2O_3$ (*1*), $Zn - CoO - Al_2O_3$ (*2*), and $MgO - ZnO - CoO - Al_2O_3$ (*3*).

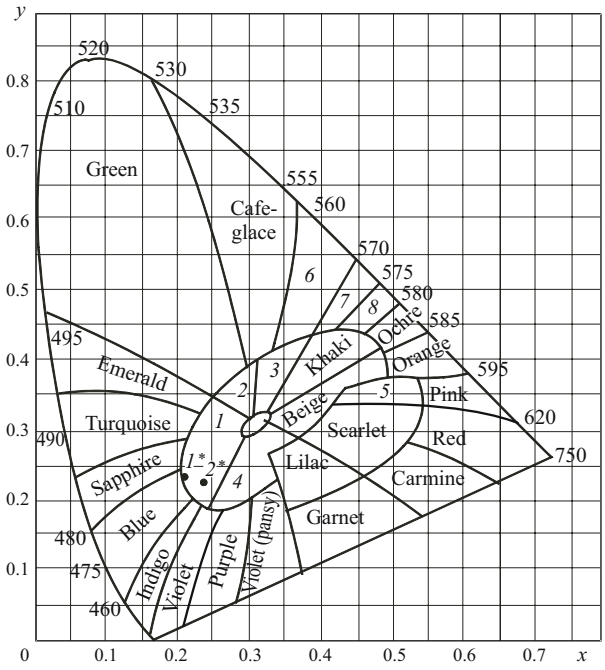

Fig. 3. Color distribution on trichromatic diagram: *1*) ultramarine; *2*) mignonette; *3*) olive; *4*) plum, *5*) salmon; *6*) yellow-green; *7*) greenish-yellow; *8*) yellow; *1**) pigment SK-1 (system $CoO - Al_2O_3$); *2**) pigment UKTs-2 (system $Zn - CoO - Al_2O_3$).

sorption bands of aluminum ions at 556 cm^{-1} in the octahedral vacancies and Co ions at 690 cm^{-1} in the tetrahedral vacancies. The vibrations of the bonds of zinc and magnesium ions in this case coincide with the vibrations of the aluminum ion bond. As a consequence of the synthesis, aluminomagnesian spinel is additionally formed:

$$MgO + Al_2O_3 = MgAl_2O_4.$$

TABLE 1

Pigment*	Chromaticity coordinates		Color characteristics (in system MKO 1964)	
	x_{10}	y_{10}	color tone, nm	color purity, %
SK-1	0.224	0.243	475	0.48
UKTs-2	0.242	0.240	472	0.38

* SK-1) blue pigment obtained in system CoO – Al_2O_3; UKTs) ultramarine pigment obtained in system ZnO – CoO – Al_2O_3.

The resulting pigment has a pale-blue shade. The absorption spectra recorded in the wavelength range of 350 – 800 nm were used to calculate the characteristics of pigment colors (Table 1), which are also represented on the chromaticity diagram (Fig. 3).

The similarity of the structures and parameters of spinel lattices facilitates the formation of substitutional solid solutions (spinelides): $CoAl_2O_4$, $ZnAl_2O_4$, $ZnCo_2O_4$, $MgAl_2O_4$ ($CoAl_2O_4$ is the main phase). The disintegration of the solid solution containing $ZnCo_2O_4$ leads to the formation of $CoO \cdot xZnO$ zones in the pigment structure. All these factors affect the final chromaticity of pigments.

Thus, spinels synthesized in the layer-by-layer combustion mode using the SHS method can be used as heat-resistant pigments of a blue-sky-blue color spectrum.

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